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# Phase Equilibrium in Amino Acid Salt Systems for CO2 Capture

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# Phase Equilibrium in Amino Acid Salt Systems for $CO_2$ Capture

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# Outline

**Introduction**

- General introduction
- Experimental data  for amino acid salt systems
- Methionine as a case study

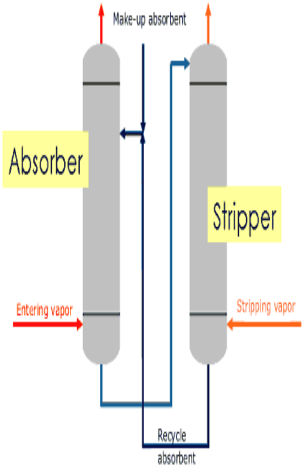
**Carbonate-Methionine system**

- Equilibrium constants
- Vapor-Liquid equilibrium data
- Freezing point depression data
- Thermodynamic modelling

**Comparison of absorbents**

- Absorber conditions
- Desorber conditions
- Heat of desorption
- Conclusion

# Introduction



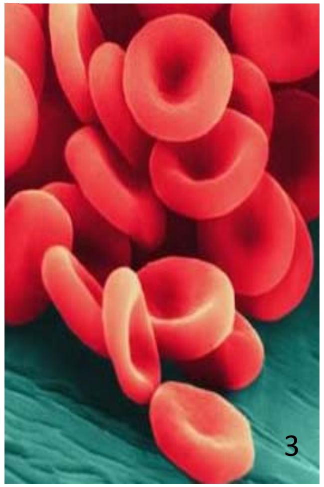

**Advantages in using amino acid salts instead of alkanolamines:**

- Might be less prone to degradation in oxygen rich environments
- Less volatile than alkanolamines due to their ionic nature
- Same affinity towards $CO_2$ as alkanolamines
- Form carbamates

Amino acids participate in the transportation of $CO_2$ in the blood by the formation of carbamate

**Problems and drawbacks:**

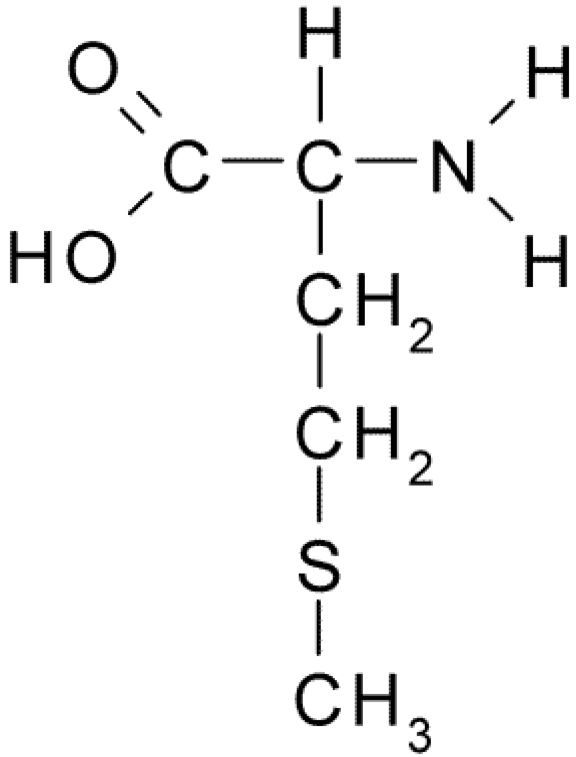
- More expensive
- Limited solubility of amino acids in water
- Limited amount of experimental data available in literature



# Experimental data for amino acid salt solutions

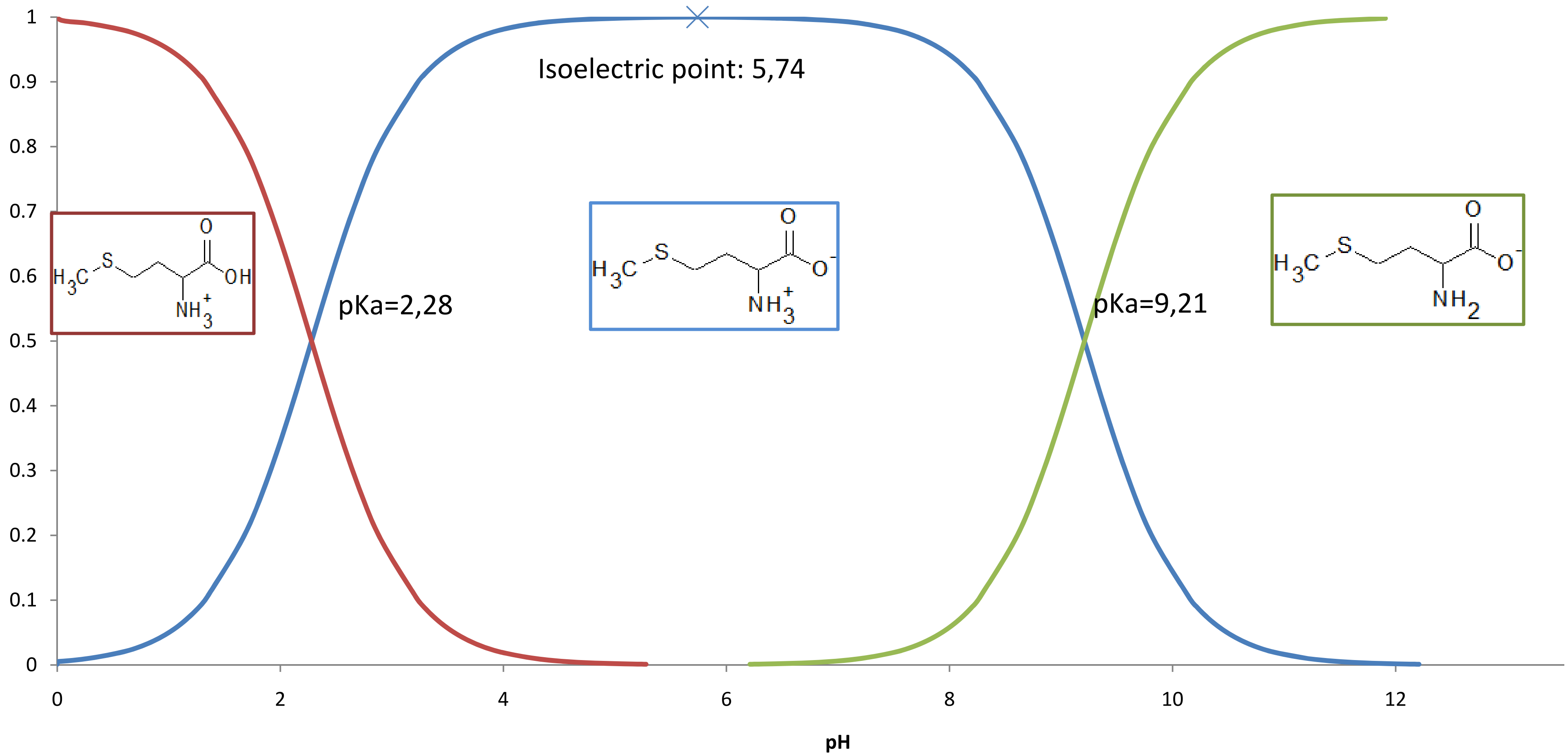
- **$CO_2$ Equilibrium data**
  - Potassium taurate – Kumar *et al.* (2003) **38 data points**, T=25 and 40°C
  - Potassium glycinate (Portugal *et al.* 2009) **103 data points**, T= 20-50°C
  - Potassium methionate (Kumelan *et al.* 2010) **65 data points**, T= 80-120°C
  - Potassium sarcosinate (Aronu *et al.* 2010) graph with 55 points, T=40-120°C
  - Potassium prolinate (unpublished, DTU, UTwente)
- **Absorption kinetics**
  - Kumar *et al.* (2003) (potassium salt of taurine and glycine)
  - Van Holst *et al.* 2009 (potassium salts of 7 different amino acids)
  - Prakash *et al.* 2010 (potassium salts of taurine and glycine)
- **Equilibrium constants**
  - Sharma *et al.* 2003
  - Hamborg *et al.* 2007
- **Heat capacity and other thermal properties - none**
- **Freezing point depression data**
  - Sengeløv (2010) (loaded and unloaded potassium salt of methionine) **20 data points** -14 to 0°C

# Methionine, $C_5H_{11}NO_2S$



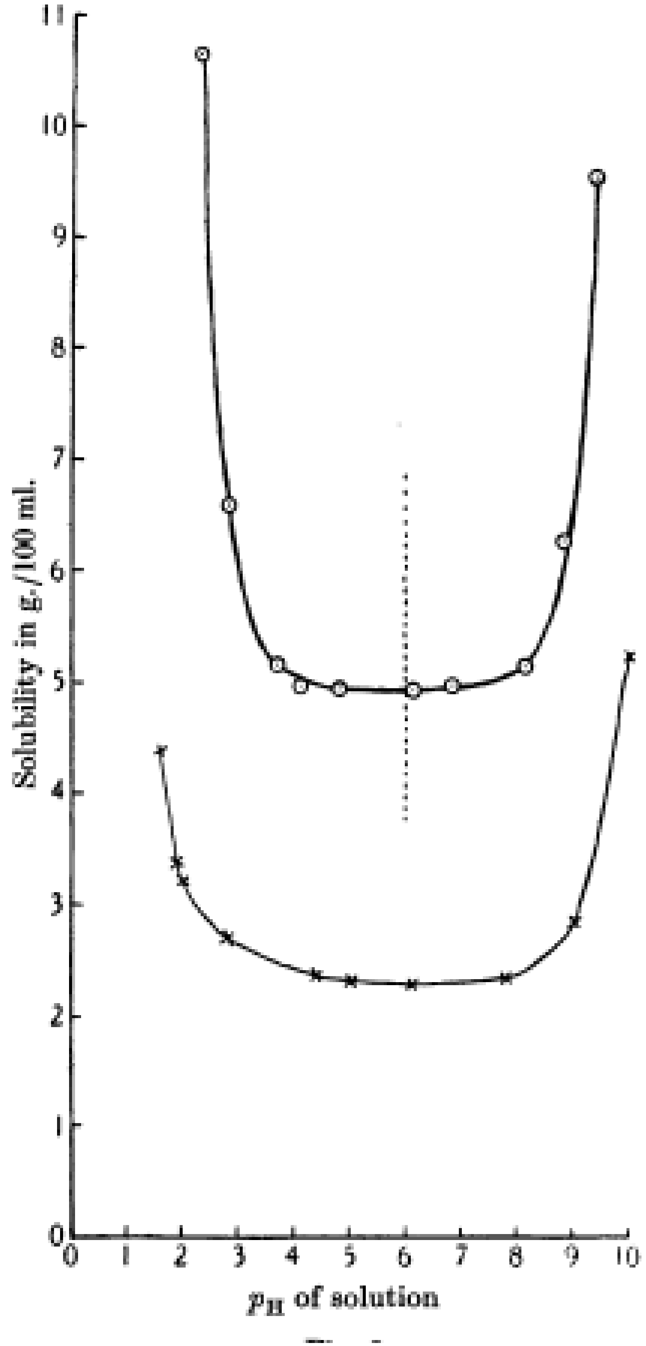

- Molar mass 149.21 g/mol
- Decomposition temperature 281°C
- Solubility in water at 25°C: 0.38 molal
- pKa 2.28 and 9.21
- Found in cereal grains and in nuts

# Iso-electric point of methionine



# Solubility of methionine in water **O** and in NaCl solution **X**

Hill and Robson, Biochemical Journal, 28(1934)1008-1013



# Potassium salt of methionine – Equilibrium constants

- Sharma VK;  Zinger A;  Millero FJ;  De Stefano C; *Dissociation constants of protonated methionine species in NaCl media*, Biophysical Chemistry, 105(2003)79-87
  - Determined in temperature range 5 – 45°C
- Hamborg ES;  Niederer JPM;  Versteeg GF; *Dissociation constants and thermodynamic properties of amino acids used in $CO_2$ absorption from (293 to 353) K*, J. Chem. Eng. Data, 52(2007)2491-2502
  - Determined in temperature range 20 – 80°C
- Equilibrium constant for the carbamate formation of methionine not available
- Equilibrium constant for the protonated form of methionine not relevant at pH above 6

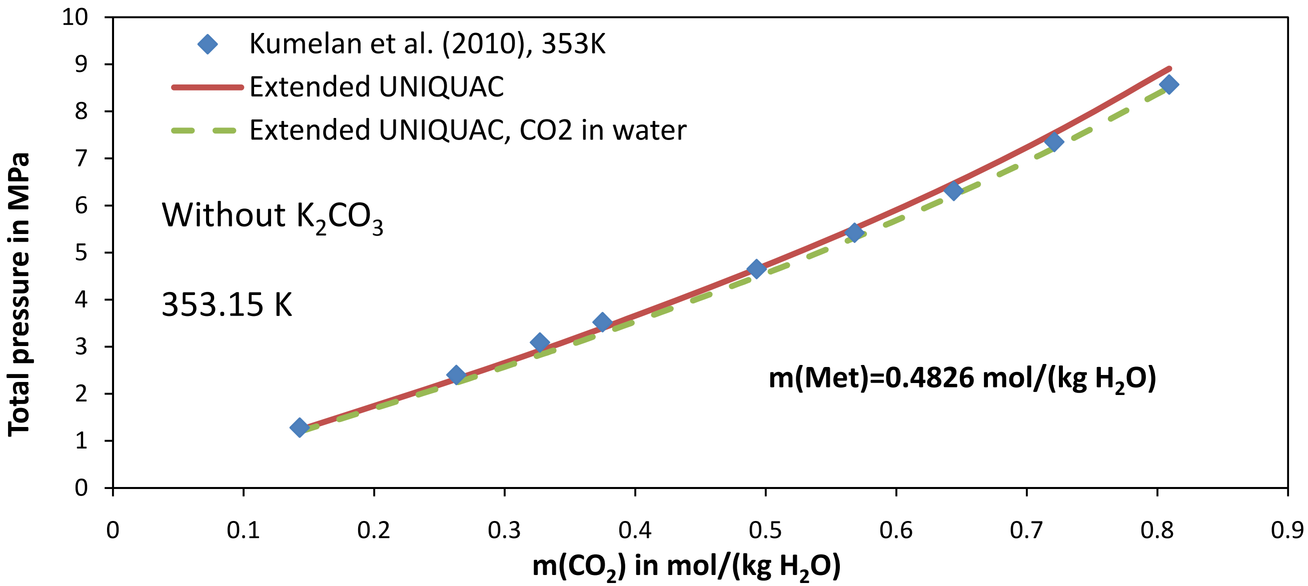
# Potassium salt of methionine – experimental data

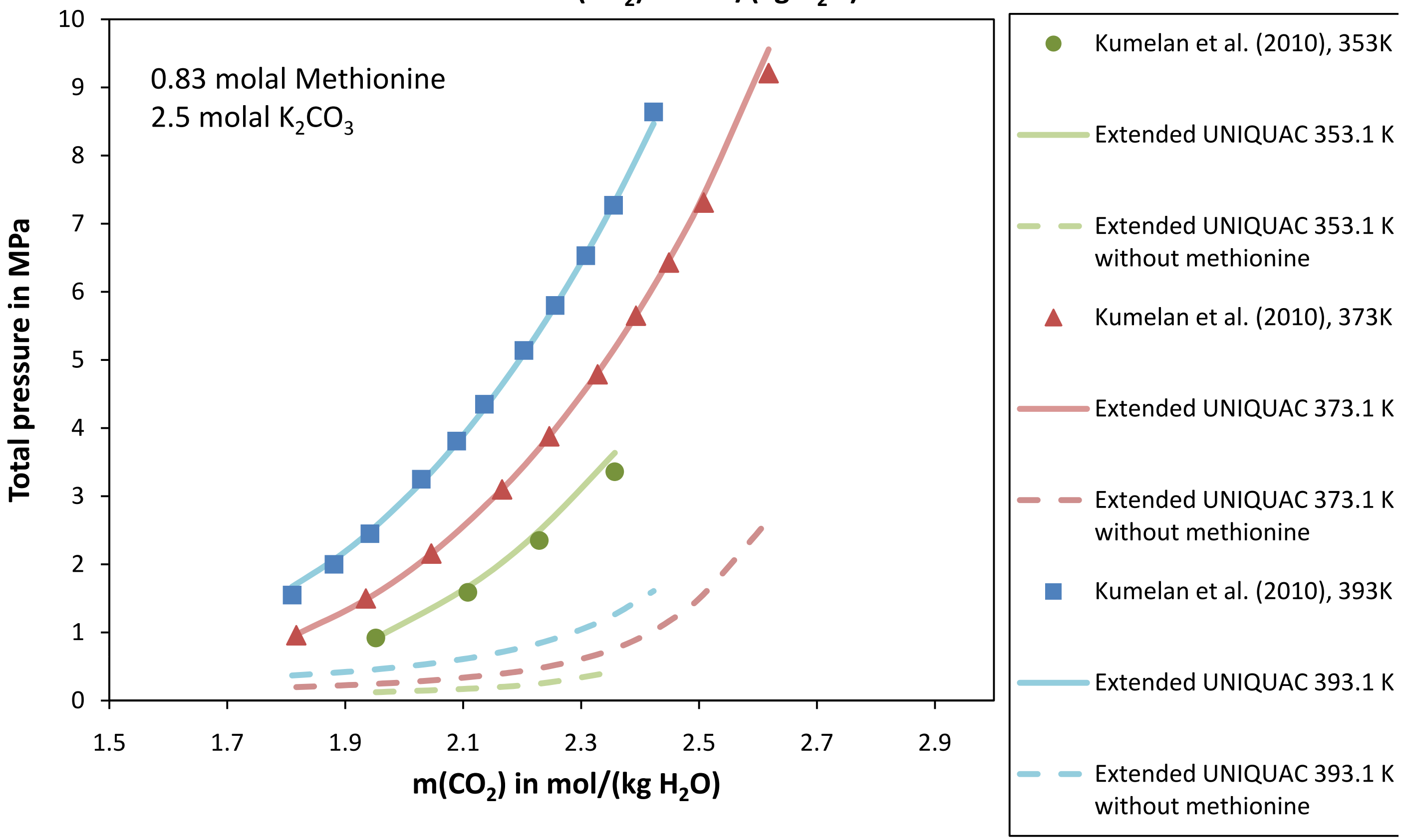
- Kumelan J, Pérez-Salado Kamps A, Maurer G, *Solubility of $CO_2$ in Aqueous Solutions of Methionine and in Aqueous Solutions of ($K_2CO_3$ + Methionine)*, Ind. & Eng. Chem. Res. 49(2010)3910-3918
  - VLE-data for the system $CO_2$-$H_2O$-$K_2CO_3$-Methionine at 80-120°C
  - It corresponds to loaded solutions of potassium salt of methionine
  - Some precipitation in experiments at 80°C with 2.5 molal $K_2CO_3$ and 0.83 molal methionine

- Sengeløv L., Bachelor Thesis, Technical University of Denmark, 2010
  - Freezing point depression data for potassium salt of methionine and for loaded solutions of this salt

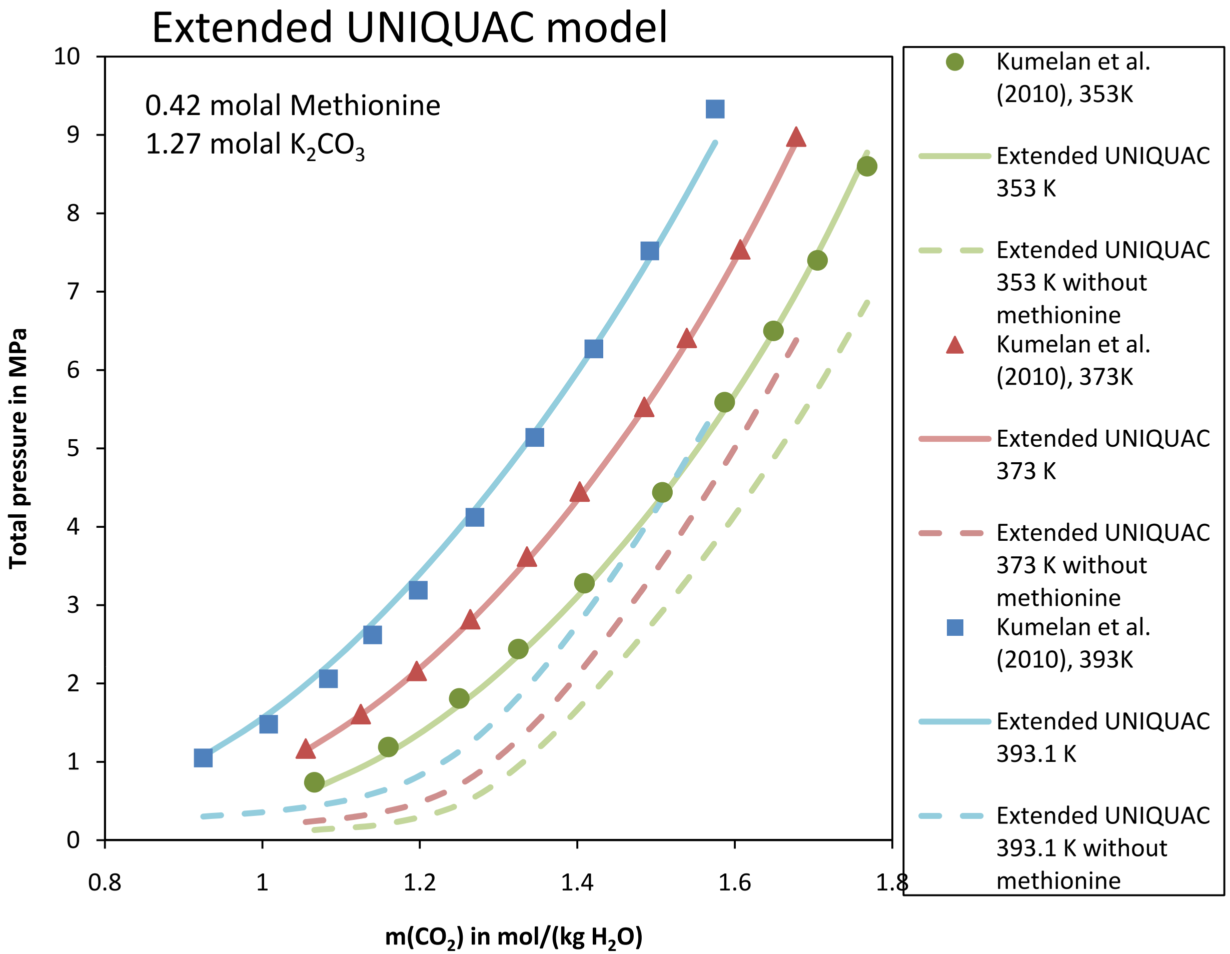
# Results for the $CO_2$-$H_2O$-$K_2CO_3$-Methionine system

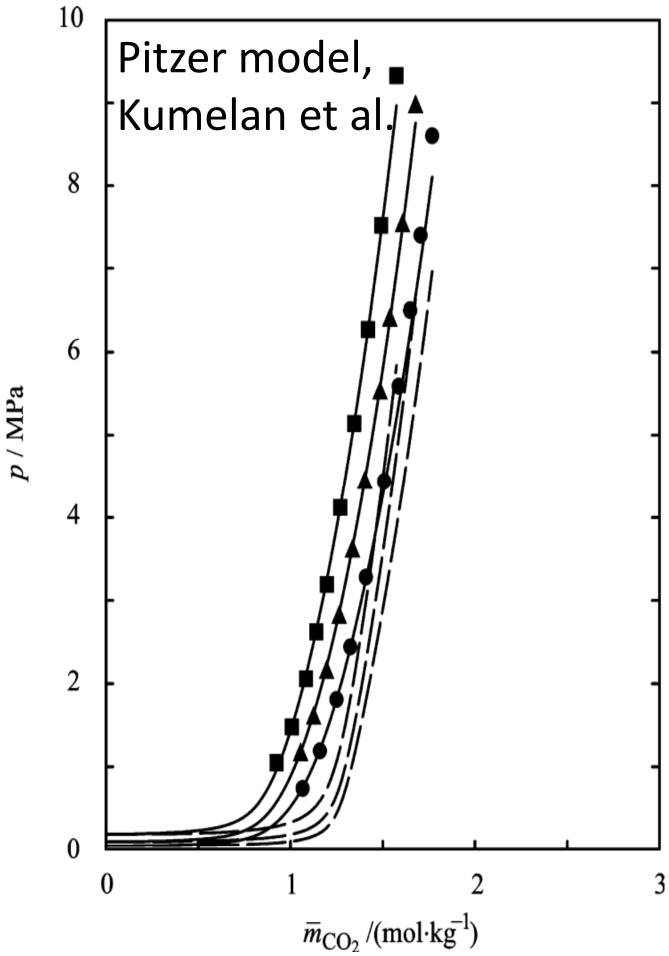
**(Eq. constant from Sharma et al.)**



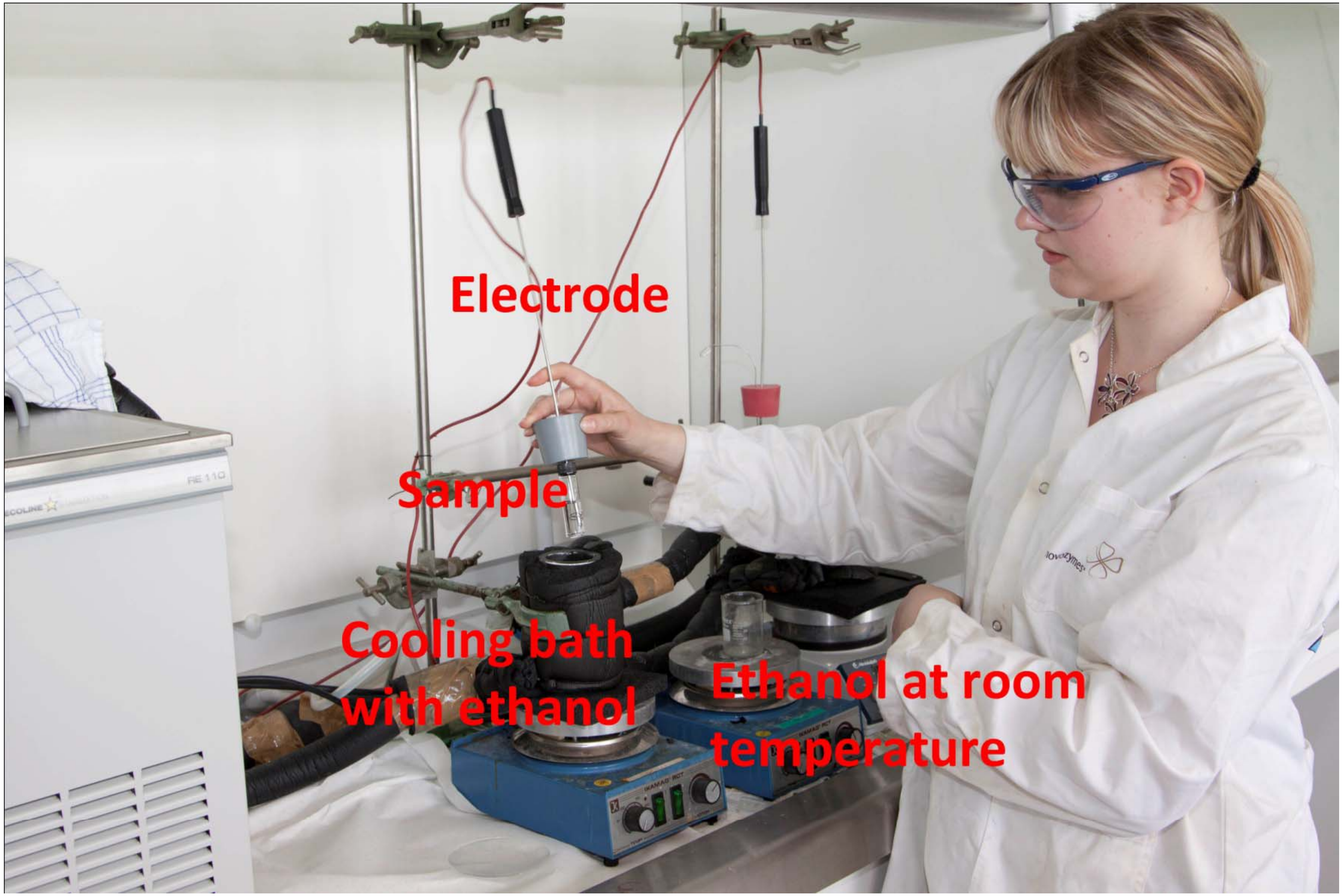
# Results for the $CO_2$-$H_2O$-$K_2CO_3$-Methionine system (Equilibrium constant from Sharma et al.)



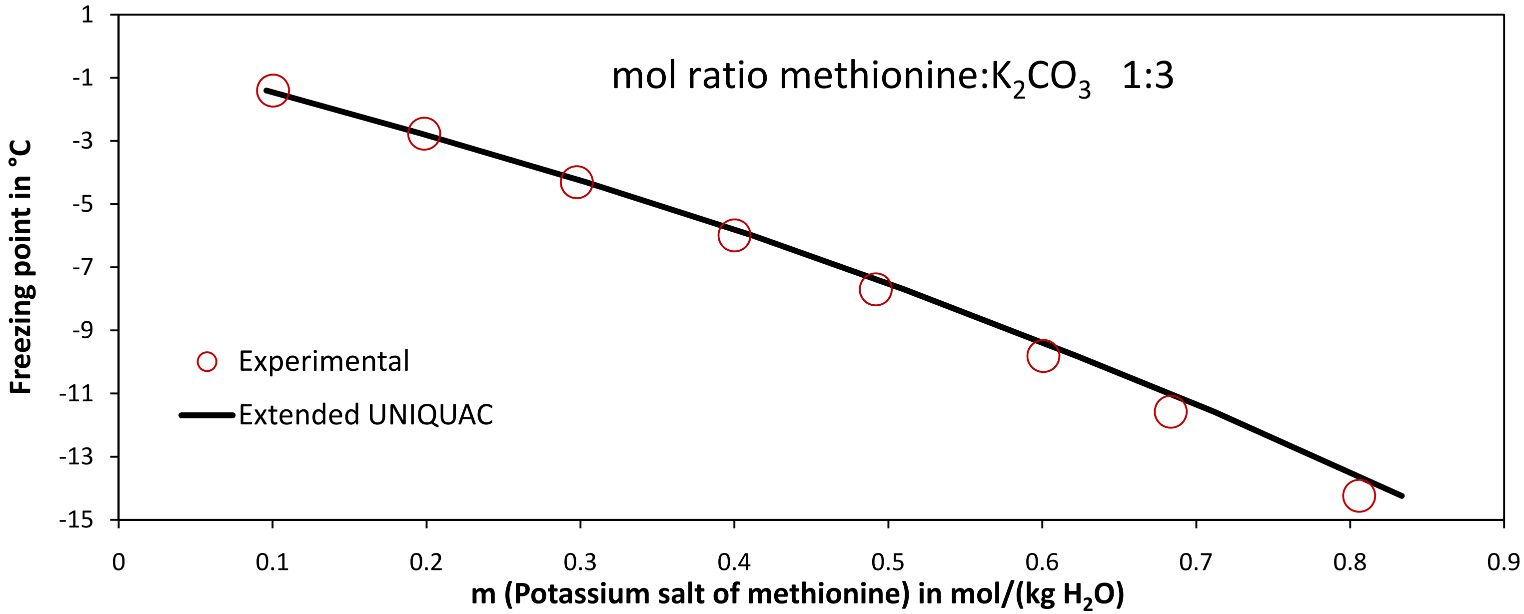



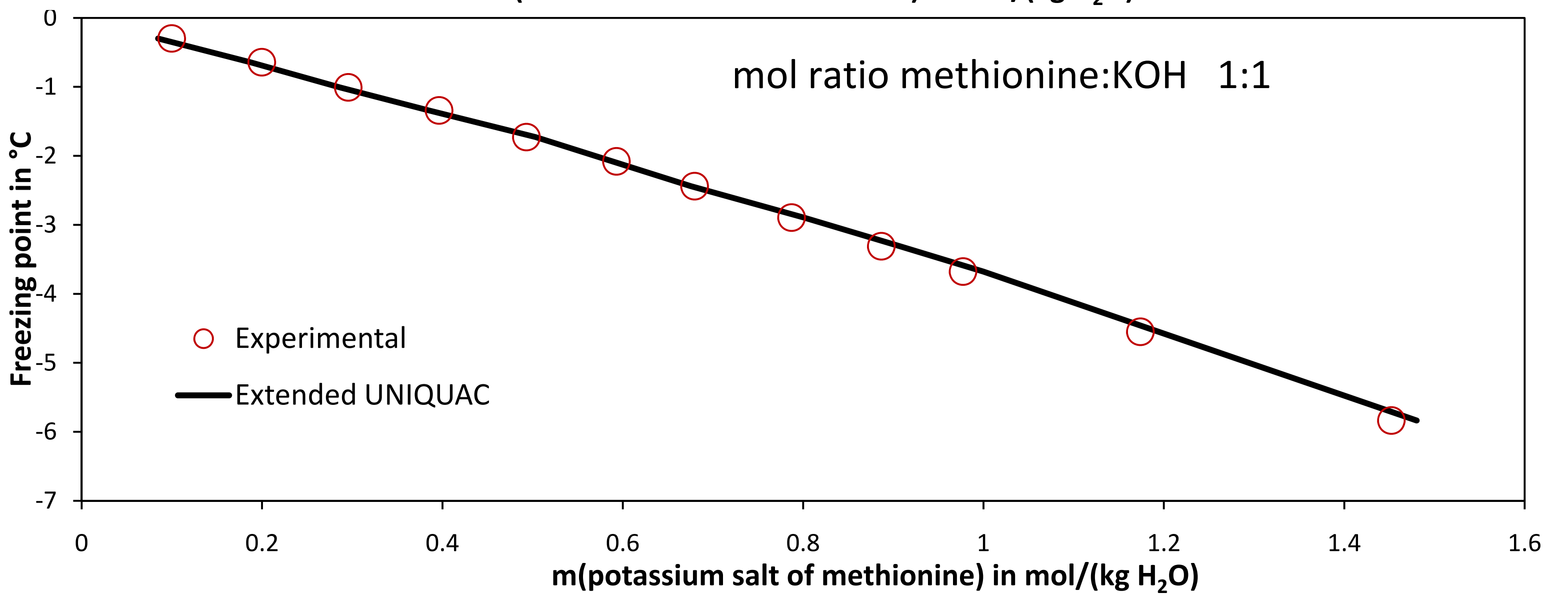

m($K_2CO_3$)≈1.27 mol/(kg $H_2O$) & m(Met) ≈0.42 mol/(kg $H_2O$)

# Measurements of freezing point depressions for mixtures of 1:1 (mole ratio) aqueous Met-KOH and 1:3 (mole ratio) aqueous Met-$K_2CO_3$



# Freezing point depressions: Results and model correlation (Equilibrium constant from Sharma *et al.*)



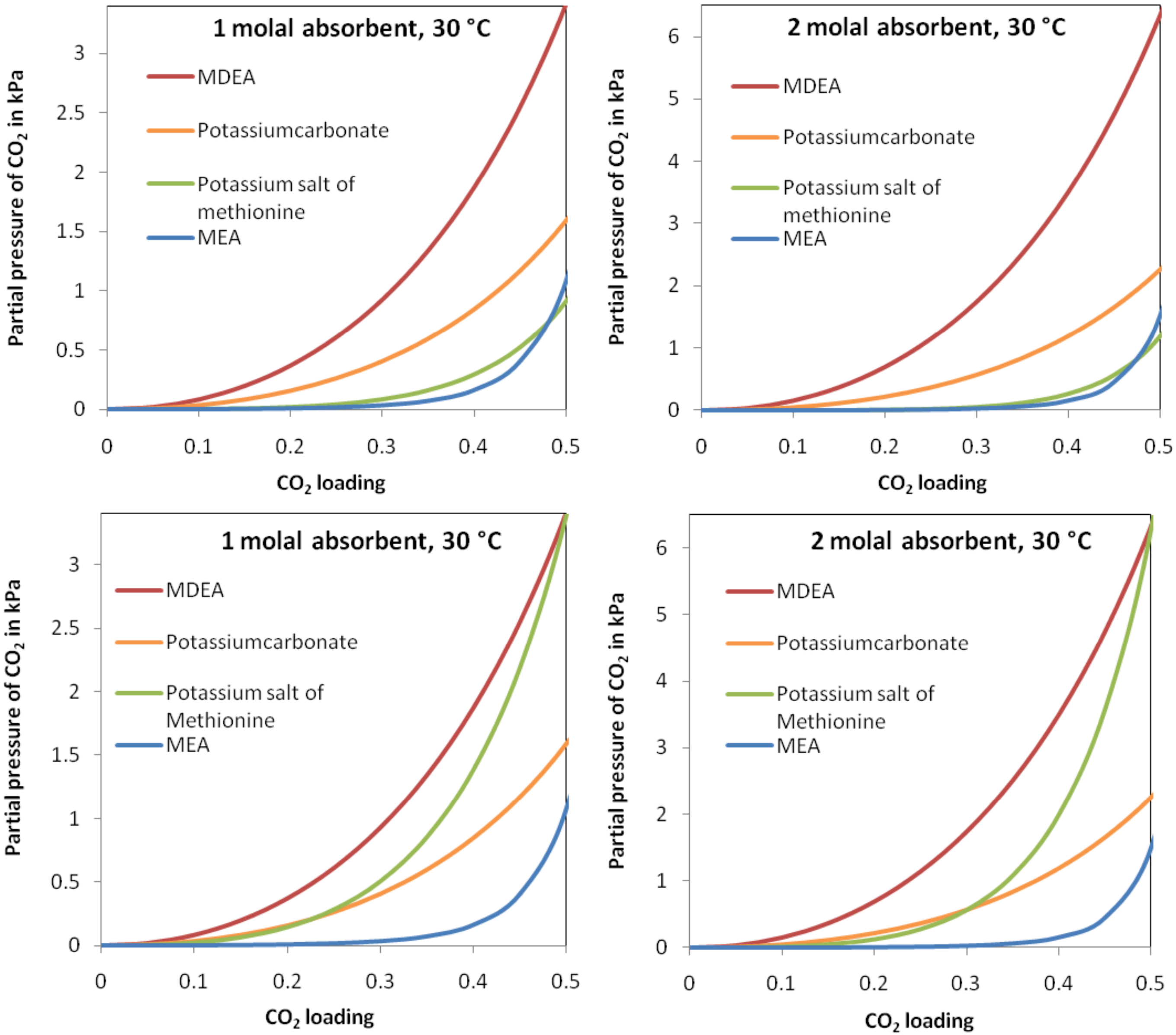



# The potassium salt of methionine as an absorbent in post-combustion contra MEA, MDEA and $K_2CO_3$

Absorber conditions

Equilibrium constant from Sharma et al.

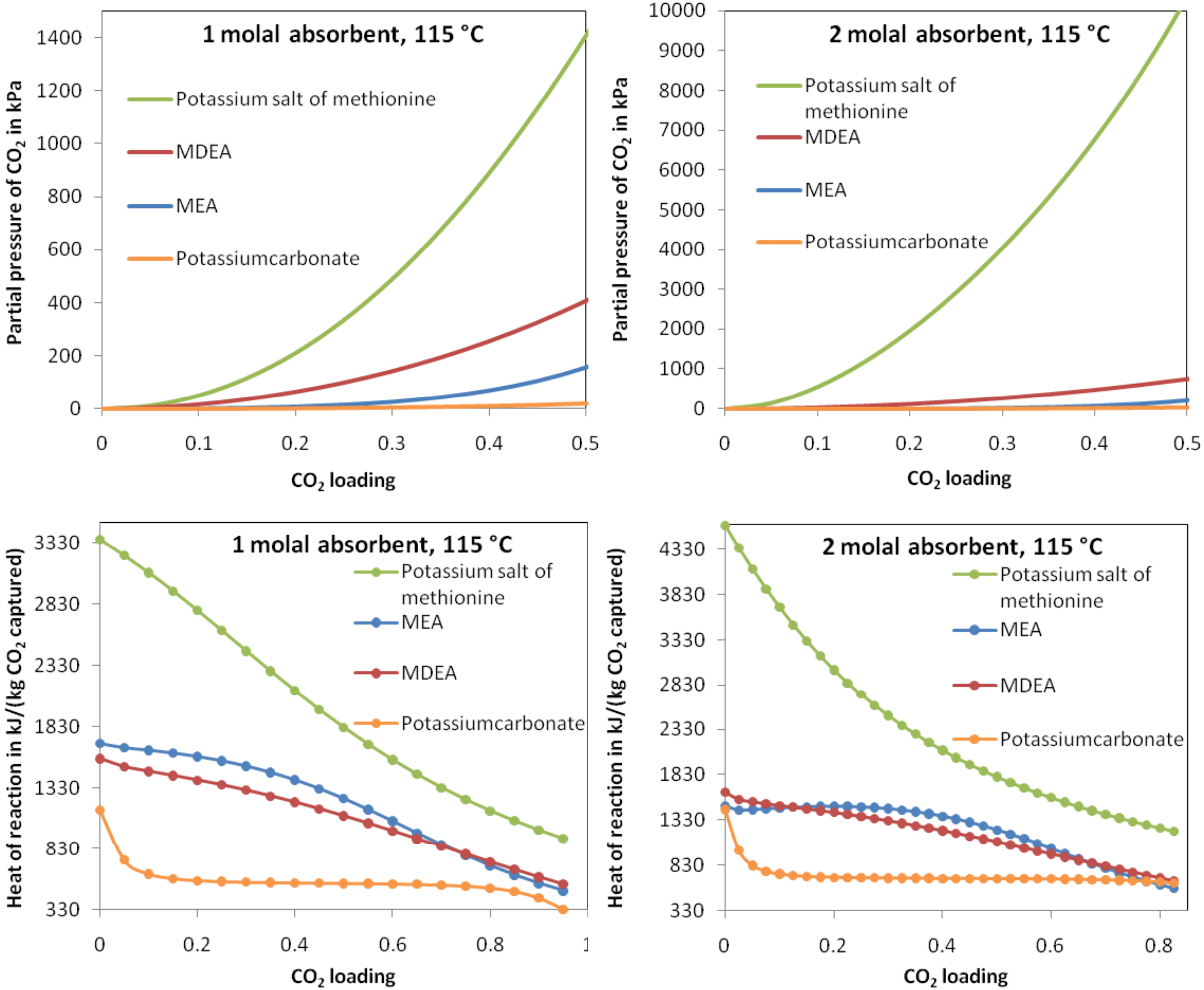
Equilibrium constant from Hamborg et al.



# The potassium salt of methionine as an absorbent in post-combustion contra MEA, MDEA and $K_2CO_3$

Desorber conditions

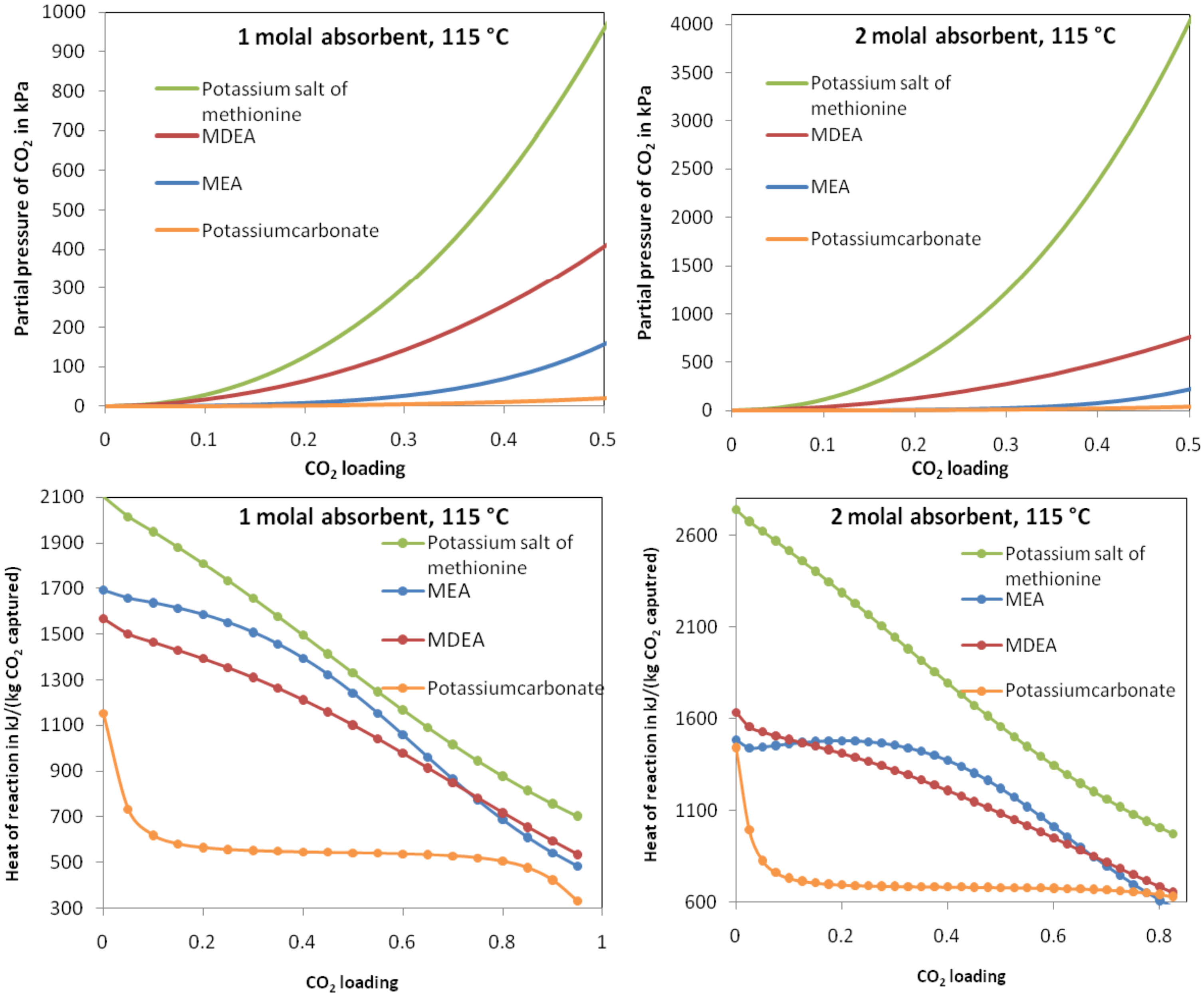
Equilibrium constant from Sharma *et al.*



# The potassium salt of methionine as an absorbent in post-combustion contra MEA, MDEA and $K_2CO_3$

Desorber conditions

Equilibrium constant from Hamborg *et al.*



# Conclusion I

- The extreme difference between the properties of the potassium salt of methionine at absorber conditions and at desorber conditions indicates:
  - A strong temperature dependence of the equilibrium constant of methionine
  - Acidic properties of methionine strongest at desorber temperature
- Portugal et al. found that the carbon dioxide solubility in potassium glycinate did not change much in the temperature range investigated (20-50°C)

# Conclusion II

- Due to the limited amount of experimental data available, it is possible to model $CO_2$ solubility in amino acid salt solutions without taking carbamate formation into account
- The potassium salt of methionine seems to have very interesting properties for post-combustion usage. However VLE-data at absorber column conditions are needed to validate the results
- The limited solubility and risk of precipitation provide challenges in the use of the potassium salt of methionine and must be investigated further
  - The 2 molal solutions for which calculations were shown here might be precipitating!
- More research is required to clarify the role of methionine in the absorption process: Especially regarding carbamate formation and kinetics
- Much more research is required on amino acid salt solutions. They have very interesting properties and could be real alternatives to alkanolamines.